

THE RAMAN SPECTRA OF ORTHO-, META-AND PARA-THIOCRESOLS

R. N. BAPAT

(PHYSICS DEPARTMENT, COLLEGE OF SCIENCE, NAGPUR)

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Plate VIII

ABSTRACT. The Raman spectra of ortho-, meta- and para-thiocresols have been studied in the present investigation. About twenty Raman lines have been recorded in the case of ortho, twelve in the case of para and about twentyfive in the case of meta- thiocresol respectively. The C-S frequency in thiocresols between 639 cm^{-1} and 685 cm^{-1} is compared with that for other mercaptans. All the three thiocresols show a strong Raman line between $1209\text{--}1223\text{ cm}^{-1}$ which is assigned to C-CH₃ stretching mode. The S-H stretching frequency lies between 2568 cm^{-1} and 2577 cm^{-1} in thiocresols. A comparison between Raman spectra of the thiocresols, phenol and thiophenol, is given in a tabular form.

INTRODUCTION

The study of the absorption spectrum of ortho-, meta- and para-thiocresols in the vapour state was undertaken to find the effect of the substitution of SH in place of OH in the three cresols, ortho, meta and para. The infrared spectra of the three thiocresols have been studied in detail. As the Raman frequencies for the three thiocresols were not reported so far, the Raman spectra of these three molecules have been studied in the present investigation.

EXPERIMENTAL

The Raman spectra of the three thiocresols were photographed on a three-prism Steinheil spectrograph. The Raman source of Steinheil consists of a horizontal mercury arc placed in a chamber cooled by circulating water through the tubes in the chamber. The light from the arc was focussed by two common paraboloid reflectors on a tube kept horizontally at their focus, the tube containing the substance under investigation. The length of the tube is about 20 cm. In between the tube and the arc was kept a filter transmitting only the 4358\AA group of radiations of mercury. Carbon tetrachloride was first distilled and collected in the tube itself and the Raman spectrum of carbon tetrachloride was first recorded (figure 1) in order to eliminate the Raman lines from this substance. Parathiocresol was next dissolved in carbon tetrachloride. The substance is very soluble and a large quantity of the substance was dissolved and the solution put in the experimental tube. It was observed that the intensity

of the Raman lines improved with higher concentrations. An exposure of three hours with this source was necessary to bring out the details in the spectrum (figure 2). Ilford HP3 Hypersensitive panchromatic plates were used to record the spectra. An iron arc spectrum was superposed in the centre, and the wavelengths of the Raman lines were calculated by Hartmann's dispersion formula using iron lines as standard. In the case of the ortho and meta thiocresols the liquids were directly distilled in the experimental tube and the Raman spectra recorded in the same manner as explained above. The wavelengths tabulated in Table I are the mean of the three readings and are accurate to $\pm 6 \text{ cm}^{-1}$. The Raman spectra of meta thiocresol and ortho thiocresol are given in figures 3 and 4 respectively.

The wavelengths of the Raman lines are given in Table I with the intensities visually estimated and having the following meaning, *v.s.* -very strong, *s*-strong, *ms*-medium strong, *mw*-medium weak, *w*-weak, *vw*-very weak and *vww*-very very weak.

TABLE I
Comparison of Raman frequencies of phenol, thiophenol
and thiocresols

Present work		Present work		Present work		Phenol (Ananth- krishnan 1936)	Thiophenol (Venkate- swaran 1930)
Ortho-thiocresol Raman	Infrared	Meta-thiocresol Raman	Infrared	Para-thiocresol Raman	Infrared	Raman	Raman
1	2	3	4	5	6	7	8
		121 vvw					
147 vw		146 vw					
233 m		177 vw				243 (-)	194 (5d)
334 w		223 mw					282 (2d)
432 m		410 w					415 (3)
500 w						—	
552 m		523 m				507 (3)	
						532 (4)	
						590 (0)	596 (0)
						620 (4)	618 (3)
661 m	676 m	685 ms	686 (s)	639 w	—	655 (00d)	695 (3)
723 w						756 (3)	730 (0b)
	772 s						
705 ms	797 m		772 vs		789 m	787 (0b)	
						812 (8)	
882 w		855 mw	853 s			830 (3)	

TABLE I (contd.)
Comparison of Raman frequencies of phenol, thiophenol
and thiocresols.

Present work		Present work		Present		Phenol (Ananth- krishnan 1936)	Thiophenol (Venkate- swaran 1930)
Ortho-thiocresol Raman	Infrared	Meta-thiocresol Raman	Infrared	Para-thiocresol Raman	Infrared	Raman	Raman
1	2	3	4		6	7	8
919 m	924 m	918 vw 942 vw	919 m		913 m		918 (4d)
968 m						991 (0)	
		1001 vs	982 m	985 m	1002 vw	1001 (10)	1000 (10)
1047 s	1046 s		1041 m	1036 w	1041 m	1027 (8s)	1024 (4)
		1084 m	1083 ms			1072 (1)	1071 (0) 1092 (3)
	1111 m	1111 m	1109 ms	1102 vs	1115 ms	1113(0)	1118 (3)
						1155 (3s)	1157 (2)
		1172 m	1168 ms			1170 (4s)	
1209 ms	1217 ms	1221 ms	1218 m	1222 m	1211 m		
	1250 vw	1276 vw	1272 vw		1232 w	1253 (21s)	
1369 r	1381 m	1383 mw	1383 w	1386 w	1379 m		1361 (1d)
						1425 (00)	
						1464 (0)	1432 (0d)
	1408 sh		1401 sh		1403 ms		
	1475 s		1479 s		1497 s	1498 ($\frac{1}{2}$)	1502 (0b)
1567 m	1577 m	1577 m	1582 s			1595 (5)	1584 (5)
1611 r	1595 m	1597 m	1603 s	1597 s	1608 vw	1605 (5)	
					1631 m		
				2492 vw			
2566 w	2577 m	2575 vw	2577 m	—	2571 w		2573 (7d)
		2870 vw					
2913 m	2941 m	2927 m	2941 m	2914 m	2924 m		2945 (1b)
						3017 ($\frac{1}{2}$ h)	
						3051 (5)	
3051 m	3067 m	3055 ms	3067 m	3051 m	3030 m	3064 (8)	3059 (8d)
		3117 vw 3176 vw		3136 w		3085 ($\frac{1}{2}$) 3150 (00d)	
						3200 (0bd)	
						3524 (00d)	

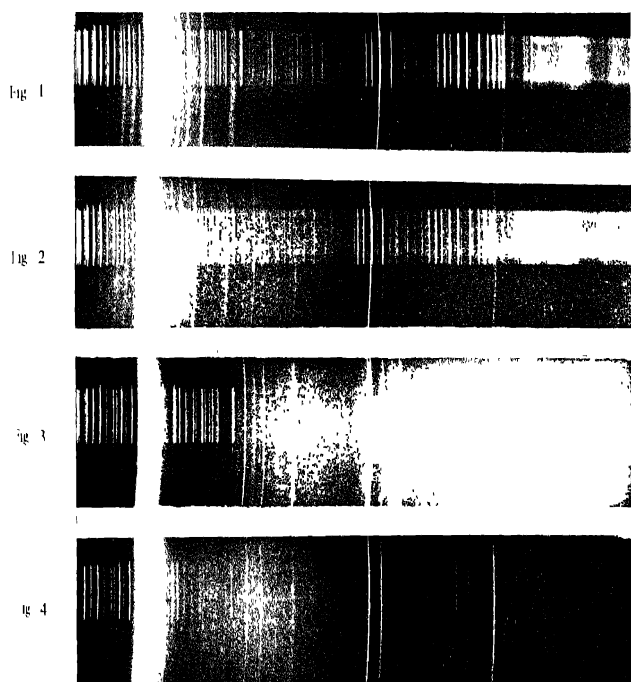
DISCUSSION

All the three isomers have certain features common in their Raman spectra. These will be discussed first. All the three thiocresols give a strong Raman line between 639 cm^{-1} and 685 cm^{-1} . The corresponding line in thiophenol is at 695 cm^{-1} . In the case of mercaptans (Sheppard, 1950) it is shown that the C-S frequency usually falls in this range. In analogy in the present case these frequencies have been assigned to C-S stretching mode. Comparison shows that there is no corresponding frequency either in toluene or phenol and hence such an assignment is justified. It may be observed that the corresponding frequencies are very strong in ortho and meta-isomers but rather weak in para-isomer. One would expect two lower frequencies arising out of the two split frequencies corresponding to 606 cm^{-1} of benzene. In thiophenol these presumably are 596 cm^{-1} and 618 cm^{-1} . In the thiocresols, however, the bands at 552 and 523 cm^{-1} in ortho and meta thiocresols respectively may be one of these, the other component being obscured by the strong C-S band.

In ortho-thiocresol there is a strong Raman line at 795 cm^{-1} which has no corresponding line in meta- and para-thiocresols. The comparison with infrared spectrum shows that there are strong infrared bands at 772 cm^{-1} and 789 cm^{-1} in the meta and para isomers. These have been assigned as corresponding to 992 a_{1g} breathing benzene vibration. The frequencies corresponding to this mode in the Raman spectra of toluene and phenol are $786, 812\text{ cm}^{-1}$. In thiophenol, however, there is no strong line corresponding to this frequency. The assignment of this frequency has been recently reviewed and it seems to be more justifiable to choose a value less than 992 according to Wilmshurst (1957) and Bernstein rather than about 1000 cm^{-1} as was done by Pitzer and Scott (1943). It, however, does not explain why this line particularly should not appear in the Raman spectra of meta and para thiocresols and phenol though there are strong bands in infrared in about the same region.

In the region around 1000 cm^{-1} there are two strong lines in toluene at 1004 cm^{-1} and 1030 cm^{-1} . Such lines in thiocresols are at 1046 cm^{-1} in *o*-thiocresol, 1001 cm^{-1} and 1084 cm^{-1} in *m*-thiocresol and 985 and 1036 cm^{-1} in *p*-thiocresol. At least three lines are expected in this region and following Wilmshurst and Bernstein, the line corresponding to 1004 cm^{-1} of toluene is assigned to 1010 b_{1u} of benzene. The other lines near 1040 and 1080 cm^{-1} are in the region where CH_3 rocking vibrations are expected. These lines are assigned as such in the Raman spectra of thiocresols.

The next strong Raman line in all the spectra of thiocresols is the strong one between 1209 and 1222 cm^{-1} . This apparently corresponds to the strong line at 1208 cm^{-1} of toluene and following the assignment in toluene it has been assigned



Raman spectra

- | | |
|---------|---|
| Fig. 1. | Raman spectrum of CCl_4 |
| Fig. 2. | " " " <i>p</i> -thiocresol (in CCl_4 solution) |
| Fig. 3. | " " " <i>m</i> -thiocresol |
| Fig. 4. | " " " <i>o</i> -thiocresol |

to C-CH₃ stretching mode. That there is no corresponding line in phenol or thiophenol substantiates such a conclusion.

All the thiocresols show a line near 1369—1386 cm⁻¹ and toluene shows a corresponding strong line at 1379 cm⁻¹. In the case of toluene it has been assigned to an internal mode arising out of methyl group corresponding to CH₃ symmetric bending. The intensity of this line is however much weaker in meta and para-thiocresols and is stronger in *o*-thiocresol.

Ortho and meta-thiocresol show Raman lines near 1570 cm⁻¹ and 1600 cm⁻¹ which correspond to two lines in toluene at 1585 and 1604 cm⁻¹. These in the case of toluene correspond to the two components of the 1596 ν_7^+ frequency of benzene. The values corresponding to these are as shown in Table II. The question of assignment of the frequencies in *p*-thiocresol is, however, doubtful. The Raman spectrum of *p*-thiocresol shows a single strong line near 1597 cm⁻¹ and the infrared spectrum two bands, a weaker one at 1608 cm⁻¹ and a stronger one 1631 cm⁻¹. It is rather difficult to choose the two bands. The most obvious choice is 1597 and 1631 cm⁻¹, but the latter frequency however seems too large as compared to that in other disubstituted benzenes. This value however seems to be in line for a trisubstituted benzene. This is however true also of *p*-xylene and this observation about the relation of split frequency as a function of position of substitution has yet to be verified.

The next strong line obviously corresponds to S—H stretching frequency and is common to all the isomers. It lies between 2566–2577 cm⁻¹ in all the cases. Here again the line is missing in the case of para thiocresol. The infrared band corresponding to this in infrared is also weak in case of para-isomer as compared to ortho- and meta-isomers. The two other bands on the higher frequency side, one near 2900 and the other near 3050 cm⁻¹ correspond to CH stretching of the methyl group and the aromatic CH stretching vibrations respectively.

It is thus observed that there are some interesting individualities in the Raman spectra of these isomers corresponding to position of substitution. It would be interesting to compare these in the corresponding cresols.

In the molecules as under discussion, a large number of vibrations are expected below 500 cm⁻¹ arising out of different bending modes specially due to substituents. In the present case about five frequencies are observed in the case of both *o*- and *m*-thiocresols. In the case of *p*-thiocresol the observations have not been extended to that region. It is rather difficult to give an unequivocal assignment of these bands, since the correlation with either the thiophenol or toluene spectrum is not possible. These low frequency vibrations in all these compounds possibly offer a fruitful subject for further investigation.

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REFERENCES

- Ananthkrishnan, R. 1936, *Proc. Ind. Acad. Sci.*, **3A**, 52.
Pitzer, K. S. and Scott D. W. 1943 *Journ. Amer. Chem. Soc.* **65**, 803
Sheppard, N. 1950, *Trans. Far. Soc.* **46** 429.
Venkateswaran, S. 1930 *Ind. J. Phys.* **5**, 219.
Wijnshurst, J. K. and Bernstein, H. J., 1957, *Canad. Journ. Chem.*, **35**, 226